

# Influence of oxygen flow and film thickness on the texture and microstructure of sputtered ceria thin films

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An in depth understanding of the influence of the deposition parameters on the texture and microstructure of sputtered ceria thin films could pave the way towards the optimization of doped ceria thin films to be applied as fuel cell related electrolytes. In this work, ceria thin films were deposited at constant current using DC reactive magnetron sputtering. The influence of the oxygen flow and the film thickness on the crystallographic orientation and microstructure was studied. 200 nm thick films exhibit a change in out-of-plane orientation from random to preferential that coincides with the transition from metallic to poisoned mode. The preferential out-of-plane orientation of the films deposited in metallic mode changes from random to [200] as a function of both thickness and oxygen flow. Hence, films deposited in this mode are identified as grown under zone T conditions which agrees with scanning electron microscopy cross sections. In poisoned mode, however, a second transition is observed. The films deposited in this mode grow in zone II, but a change in preferential out-of-plane orientation from [200] to [111] occurs when increasing the oxygen flow to higher values.

## 1. Introduction

The complex oxide materials used as oxygen ion conductor in traditional solid oxide fuel cells (SOFC) demand a high working temperature of the fuel cell and as such impose strong material restrictions [1]. This limits not only the applicability of SOFCs, but also adds to the cost price. A lower operational temperature would offer the economical advantage of replacing the expensive ceramic parts of these cells by cheaper metallic alternatives. Degradation of the electrolyte, the reaction of the electrolyte with other cell components and thermal mismatch between the different parts of the fuel cell would be minimized as well [2, 3].

At present, the expected performances of fuel cells are not yet proven. Especially in terms of lifetime, maintenance and reliability there are still many unknowns. One of the main drives in current research is to lower the working temperature which would lead to a better integration of solid oxide fuel cells [4]. To do this, a better and thinner electrolyte is needed. One material meeting this demand is doped  $\text{CeO}_2$  which has a higher ion conductivity than YSZ at low temperatures [5, 6]. By downscaling the electrolyte to a thin film ( $< 5 \mu\text{m}$ ), and therefore minimizing ohmic resistance, the structure and characteristics of the electrolyte are changed due to the occurrence of small scale or nano effects [7].

A full understanding of the influence of the deposition conditions on the texture and microstructure [8] in sputtered cerium oxide thin films could be a first incentive towards the optimization of (un)doped ceria thin films to be applied as electrolyte in conventional fuel cells [9] or battery replacements [10], and in oxygen sensors [11, 12]. In this study ceria thin films were deposited by reactive magnetron sputtering [13], a physical vapour deposition (PVD) technique, and their structure was characterized as a function of oxygen flow [14] and film thickness.

## 2. Experimental setup

Ceria thin films were deposited at a constant current of 0.25 A using DC reactive magnetron sputtering. A cerium target (99.5 % purity; Testbourne Ltd), 50.8 mm in diameter and 3 mm in thickness, was clamped on an unbalanced magnetron inside a rectangular cuboid vacuum chamber. The magnetron was positioned 115 mm away from a rotatable substrate holder. A shutter was installed between magnetron and substrate to sputter clean the target before each deposition. The chamber itself was pumped down to a background pressure below  $3.5 \times 10^{-4}$  Pa using a turbo-molecular pump and a rotary pump. The pressure was adjusted to 0.5 Pa by introducing between 33 and 37 sccm of Ar into the chamber and maintaining a pumping speed of approximately 109 L/s. Oxygen was brought directly to the substrate via a local and branched inlet to maximize film oxidation while minimizing target oxidation [15]. Amorphous glass substrates (26 mm x 12.5 mm) were first cleaned with distilled water and subsequently by ultrasound in methanol.

Fully transparent  $\text{CeO}_2$  films with different textures and microstructures were obtained at different oxygen flows and thicknesses. The sputtering time was chosen according to the desired thickness. Typical deposition rates in metallic mode ranged from 23.5 to 27.5 nm/min and in poisoned mode from 0.5 to 4 nm/min. The thickness of the deposited films was measured with contact profilometry (Taylor-Hobson Talystep), and double checked by cross section scanning electron microscopy (SEM). Chemical surface analysis was performed with X-ray photoelectron spectrometry (XPS) using monochromatic Al  $K\alpha$  X-rays. A pass energy of 56.1 eV was applied. An electron flood gun at 4 eV was employed. The thin film texture was

determined with X-ray diffraction (XRD), based on Cu K $\alpha$  radiation, in the Bragg-Brentano setup using a LynxEye Silicon Strip detector. The microstructure of the ceria thin films was assessed by scanning electron microscopy (SEM) with a high voltage of 20 kV and a spot size of 3.0. To reduce surface charging, a thin Au film was deposited before the analysis. The energy flux was measured with a passive thermal probe at the experimental conditions under which the films were deposited [16].

### 3. Results

#### 3.1. Selection of the deposition conditions

The cerium oxide thin films were deposited with reactive magnetron sputtering. Cerium is DC sputtered from a metallic target and a reactive gas, oxygen in this case, is introduced into the vacuum chamber through a local and branched inlet. The intrinsic disadvantage of this process is that the oxygen does not only react with the cerium on the substrate but also with the metallic cerium target [13, 17]. This causes process parameters such as the partial pressure of the oxygen gas, the discharge voltage and the deposition rate to change in a non linear fashion as a function of the reactive gas flow. Fig. 1 shows the hysteresis behaviour of the discharge voltage measured at constant current as a function of increasing and decreasing oxygen flow. Depositions were done along the increasing flow curve to study the influence of the reactive gas on the structure of the cerium oxide thin films. In metallic mode, where the deposition rate is high because the target surface remains metallic, the oxygen flow was varied from 0 to 1.5 sccm in steps of 0.5 sccm. The transition from metallic to poisoned mode, characterized by a sudden drop in discharge voltage and

deposition rate, occurs at an oxygen flow of 1.9 sccm. In poisoned mode, where compound formation prevails at the target surface, the flow was varied from 2.0 to 5.0 sccm. Parameters such as the discharge current (0.25 A), the target-substrate distance (115 mm) and the argon pressure (0.5 Pa) were kept constant during the depositions.

### 3.2. Influence of the film thickness and oxygen flow on texture and microstructure

Fig. 2 shows the XRD diffraction patterns of the ceria films grown at different O<sub>2</sub> flows chosen along the increasing flow curve of the above described hysteresis. According to the resulting diffraction spectra, crystalline films were obtained. The lines of the diffraction peaks correspond with those of cubic CeO<sub>2</sub> (JCPDS card file 34-0394) which is in line with XPS results (not shown here) confirming a O:Ce ratio of approximately 2:1. These films have a thickness of around 200 nm. In order to more clearly visualize the texture changes occurring in the thin films, the XRD intensities were corrected for their respective thickness. The main crystallographic orientations, being [200], [111] and [220], were then determined by normalizing the net area of the intensity peaks with respect to the powder diffraction intensities. For example, the [200] fraction of crystallites is given by

$$F_{200} = \{A_{200}/I_{200}\} / \{A_{200}/I_{200} + A_{111}/I_{111} + A_{220}/I_{220}\} \quad (1)$$

with A<sub>i</sub> being the net peak area and I<sub>i</sub> the relative intensity given by the JCPDS card file.

The result of this calculation is shown in fig. 3. For a 200 nm thin film, the out-of-plane orientation is not yet preferential but random in metallic mode or for low oxygen flows (see fig. 3a). A mixture of the three main fractions, being [200], [111] and [220], is obtained. It is seen that when the oxygen flow is varied from 0.5 to 1.5 sccm, the [200] fraction decreases. Once poisoned mode is attained, the thin films grow with a [200] preferential out-of-plane orientation. The [200] fraction reaches its highest value at 2.5 sccm. As the oxygen flow is increased further, the [200] fraction abruptly decreases and becomes negligible. [111] succeeds as the highest fraction in poisoned mode at oxygen flows of 3 sccm and higher. The [220] fraction is also present but steadily decreases for higher oxygen flows.

The thickness was varied from 200 nm to 800 nm in steps of 200 nm by adjusting the deposition time. In metallic mode the films are no longer randomly oriented at 400 nm but show a [200] out-of-plane orientation. This preferential out-of-plane orientation is even more pronounced at 600 and 800 nm, indicating that an overgrowth mechanism occurs in metallic mode [18]. Or in other words, [200] overgrows the other crystallographic orientations, namely [111] and [220], as a function of thickness. Depending on the administered oxygen flow, this overgrowth mechanism also seems to be happening faster at slightly higher oxygen flows. In poisoned mode no overgrowth takes place. For films ranging in thickness from 200 nm to 600 nm, either a [200] or [111] out-of-plane preferential orientation is found depending on the oxygen flow.

Scanning electron microscopy was employed to determine the film microstructure. The films deposited in metallic mode are characterized by V shaped crystalline columns (see fig. 4a). In poisoned mode the microstructure changes and more straight crystalline columns are formed (see fig. 4b).

### 3.3. Energy flux measurements

The experimental conditions under which the cerium oxide thin films were deposited have an influence not only on the texture but also on the microstructure of the growing film. The extended structure zone model (ESZM) describes the evolution of the microstructure of a growing film as a function of the adatom mobility [18, 19]. The adatom mobility is primarily influenced by the available energy per adatom arriving on the growing film or surface (= EPA) [20, 21]. This structure zone model consists of six zones. Films grown under zone T or zone II conditions have an out-of-plane orientation that is not random but preferential. The out-of-plane orientation in zone T is the fastest growth direction while in zone II it is the plane with the lowest surface energy. The latter is characterized by a higher grain boundary mobility, and hence a higher available energy per arriving adparticle. To determine the available energy per arriving adparticle, the total energy flux towards the substrate was measured along the increasing flow curve of the hysteresis, using the passive thermal probe. From fig. 5 it can be seen that the total energy flux is slightly higher in poisoned mode than in metallic mode. The metal particle flux towards the substrate was calculated from the deposition rate using the bulk density of cerium oxide [22]. The ratio of both fluxes yields the available energy per arriving adparticle or the EPA. Fig. 6 clearly shows that when going from metallic to poisoned mode the EPA becomes about five times as high.

### 4. Discussion

The microstructure characterized by SEM corresponds with zone T for the metallic mode (see fig. 4a). This is further substantiated by the clear overgrowth noticed in XRD as a function of the film thickness (see fig. 3), resulting in a pure [200] out-of-plane oriented thin film. Also, the low EPA gives evidence for zone T conditions [18, 19]. Indeed, grains with different orientations initially coalesce in this zone but as the film becomes thicker, they are overgrown by geometrically faster growing grains. Based on our analysis, the fastest growth direction for these  $\text{CeO}_2$  films seems to be the [200] out-of-plane preferential orientation.

In poisoned mode this evolutionary overgrowth mechanism is not seen and both thin and thick films have the same preferential orientation. Together with the microstructure analysis (see fig. 4b), this lets us to conclude that these films grow under zone II conditions. The much higher EPA supports this conclusion. According to the extended structure zone model, zone II is characterized by an out-of-plane orientation that renders the lowest surface energy for the film. For a fluorite structured material such as cerium oxide, [111] is reported to be the crystallographic orientation with the highest number of nearest neighbours and hence, the lowest surface energy [23]. In poisoned mode at higher oxygen flows, the thin films grow - as expected - with a [111] out-of-plane orientation (see fig. 3a). However, this is not the case for the deposition conditions with an oxygen flow close to the critical point where [200] is the out-of-plane preferential orientation. This behaviour is remarkable because of the following reasons. Firstly, the EPA reaches the highest values under these conditions, which favour zone II growth. Secondly, the microstructure (not shown here) is typical for zone II, and finally the texture evolution, i.e. no influence of the film thickness, also corresponds with a zone II behaviour. Under these conditions (111) should be the plane with the lowest surface energy yet fig. 3 contradicts this. From



fig. 6, it can also be seen that at 2.0 sccm of oxygen the EPA is particularly high. This in itself is an indication that the deposition conditions in poisoned mode close to and further away from the critical point are not alike. Since this second transition occurring within poisoned mode cannot be explained yet, it will be the focus of further research into the growth of sputtered cerium oxide thin films.

## 5. Conclusion

The texture and microstructure of sputtered  $\text{CeO}_2$  thin films was investigated at different oxygen flows and thicknesses. The process parameters were determined by measuring the hysteresis behaviour of the discharge voltage as a function of the oxygen flow. Thin films of cerium oxide were deposited alongside the increasing oxygen flow curve. For equally thick films, i.e. about 200 nm, a transition from random to a preferential orientation occurs as a function of increasing oxygen flow. However, once the films are sufficiently thick in metallic mode, [200] overgrows all other crystallographic directions present and becomes the out-of-plane preferential orientation. This evolutionary overgrowth mechanism seems to happen relatively faster for slightly higher oxygen flows. The determination of the available energy per adatom combined with scanning electron microscopy cross sections confirms that the transition from metallic to poisoned mode is *in se* a transition from zone T to zone II. In poisoned mode it is observed that a second transition takes place. The films show a [200] preferential out-of-plane growth at flows close to the critical point, but this preferential orientation changes at an oxygen flow of 3 sccm from [200] to [111]. Further away from the critical point, the films continue to grow in zone II with an expected [111] out-of-plane preferential orientation. More detailed research is

needed to determine the origin of this double transition seen for CeO<sub>2</sub> thin films grown along the increasing flow curve of the hysteresis.

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Fig. 1. Process curves of the discharge voltage as a function of increasing and decreasing O<sub>2</sub> flow, measured at a constant current of 0.25 A and an argon pressure of 0.5 Pa (the pumping speed was fixed at 109 L/s).

Fig. 2. XRD theta – 2 theta diffraction patterns of 200 nm CeO<sub>2</sub> thin films deposited at different O<sub>2</sub> flows. The lines correspond with those of cubic CeO<sub>2</sub> (JCPDS card file 34-0394).

Fig. 3. Calculated fractions of the main crystallographic orientations of the CeO<sub>2</sub> films with thickness a) 200 nm, b) 400 nm, c) 600 nm and d) 800 nm according to equation (1). The red line indicates the transition point between metallic and poisoned mode as shown in fig. 3a.

Fig. 4. SEM cross section of a 200 nm film deposited in a) metallic mode at 0.5 sccm O<sub>2</sub> and b) in poisoned mode at 5.0 sccm O<sub>2</sub>.

Fig. 5. The metal particle flux, derived from the deposition rate, and the total energy flux, measured with a passive thermal probe, towards the substrate or growing film as a function of the O<sub>2</sub> flow. The red line indicates the transition point between metallic and poisoned mode as shown in fig. 3a.

Fig. 6. The available energy per arriving adparticle (= EPA) as calculated from the metal particle flux, and the total energy flux (see figure 5) as a function of the O<sub>2</sub> flow. The red line indicates the transition point between metallic and poisoned mode as shown in fig. 3a.